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CONTINUOUS CASTING OF EUTECTIC FIBER COMPOSITE SHEETS

by

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ROBERT P. DICKENSON, LT., USCG

Submitted to the Department of Naval Architecture and Marine Engineering on 23 May 1969 in partial fulfillment of the requirements for the Master of Science Degree in Ocean Engineering and the Professional Degree, Naval Engineer.

ABSTRACT

The purpose of this investigation was to determine the feasibility of unidirectionally solidifying the Al-Al_3Ni eutectic at high rates by a continuous casting process and achieve a composite form. Methods of accomplishing this which were attempted included drawing the molten alloy through a cooled die, pressure forcing it through a cooled die, forcing it through a heated stream-shaping slot into water, withdrawing the molten alloy from the furnace by its adherence to steel and stainless steel strips, and drawing a mold containing the alloy through a furnace and then immediately through a cooling chamber. Although no success was achieved in forming a composite by the first four procedures mentioned above, a composite was formed at a rate of 95 cm./hr. using the fifth procedure. This success indicates promise for the continuous casting process in production of eutectic composites, particularly by the first mentioned process.

Thesis Supervisor: J. W. Mar

Title: Professor of Aeronautics and Astronautics

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I. INTRODUCTION

As designs and projects become more and more intrepid in aerospace, hydrospace, and other arenas, the quest for stronger and lighter materials has intensified. Prominent among prospects for these higher performance applications are composites. Both plastic and metal matrix composites have found acceptance in certain applications but quite slow and exacting production techniques have hampered widespread use of the metal matrix composites.

The metal matrix group generally consists of a reinforcing phase of fibrous, plate-like, or lamellar morphology surrounded by the metal matrix. Reinforcing fibers with strength on the order of 10^6 PSI are often used and, conforming to the rule of mixtures, produce composites of great strength. The strength is dependent on the alignment, size, and volume fraction of the reinforcing phase. The methods employed to form these fiber composites are generally: a) sintering or hot pressing, b) liquid metal infiltration, and c) growth from the melt of eutectic alloys by directional solidification.[1]

This paper will deal with a directionally solidified eutectic composite, the alloy of aluminum and nickel which has an eutectic composition of 6.13 wt. % nickel. When cooled directionally from the melt, this eutectic alloy forms fibers of the intermetallic compound Al_3Ni within the aluminum matrix, and these fibers are in

good alignment if plane front solidification is achieved. This composite has several appealing mechanical qualities such as a tensile strength which is more than 300% greater than the normally cast alloy[2], very good stability at elevated temperatures, a low creep rate, good toughness as a result of the ductile matrix, and formability if rolled in a direction transverse to the fiber axis[3].

Although many investigators have produced the Al-Al_3Ni composites, the growth rates employed, were generally quite slow---usually less than 30 cm./hr.[4,5,6]. In their study of composite growth from alloys of other than eutectic composition Mollard and Flemings[1] have shown that to achieve solid-liquid interface stability, the ratio of imposed temperature gradient in the liquid (G) over the rate of growth (R) must be kept equal to or greater than a constant which is dependent on the slope of the liquidus of the phase diagram at the eutectic point, the difference of the alloy composition from eutectic, and the diffusion constant of the alloy. Their experiments with alloys of the Pb-Sn system showed that samples grown below the predicted G/R critical value exhibited a dendritic structure whereas those grown above it were fiber or lamellar composites.

This work involves the determination of the feasibility of the production of Al-Al_3Ni composites at high growth rates by a continuous casting process. Mollard and Flemings' work indicate

that it should be possible to grow the composite at much higher rates than has been done previously if a high enough temperature gradient in the liquid can be achieved. A uniform temperature profile across the cross-section of the solidifying alloy is required to achieve plane front solidification. To realize this the growth of the composite in thin strip form was chosen. The production of the composite in sheet form would allow lamination of the sheets in various orientations to provide enhanced strength characteristics in all or in more than one direction.

II. EXPERIMENTAL PROCEDURE AND RESULTS

1. Water Cooled Die.

The material used in this investigation was that unused portion from the work of W. L. Marsh[5]. Details of preparation and purity may be found in his writing.

The 6.13 wt. % nickel-aluminum alloy was melted in a graphite crucible set above a water cooled graphite die as described in the appendix. A folded aluminum foil starter strip of about 0.030" thickness was placed in the 0.040" slot of the die, extending slightly up into the crucible. Below the die, the starter strip was placed between the motor driven, spring loaded rollers. An air atmosphere existed above the melt at all times. The furnace, described in the appendix, was energized and brought up to temperature and was allowed to stabilize for about 1/2 hour, the rollers were started, and the starter strip withdrawn at a rate of about 30 cm./hr. The intent in passing water through the graphite along both faces of the slot was to achieve uniform temperature across the cross-section of the metal in the slot as mentioned in the introduction. It was expected that the portion of the die extending into the furnace would be furnace heated sufficiently to keep the molten alloy above the liquidus until it had passed well into the slot.

No success was achieved in producing thin strips of the

aluminum-nickel alloy by this procedure. The portion of the foil starter strip which protruded above the die into the crucible melted as was expected. When the rollers were started however, only the unmelted portion of the starter strip was withdrawn. None of the molten alloy followed it through the die. This result persevered through furnace temperatures to 800°C and the use of a strip of 0.032 in. aluminum shim stock in lieu of the folded foil starter strip. Upon disassembling the die it was found that the molten alloy had flowed into the slot of the die less than 0.1 inch, and then not uniformly across the slot.

2. Water Cooled Die; Pressure Forced.

The same procedure that was described under procedure (1) was employed except that a graphite piston was fabricated and inserted into the top of the crucible, and connected to a 5 lb. weight above by a 3/8" steel rod threaded into the piston. When the furnace temperature had stabilized, the rollers were started as before and simultaneously the piston was lowered to bear on the top of the melt.

This procedure produced a lack of success similar to procedure (1). Again the melt protruded only a slight amount into the die. As a result of the pressure on the melt however the liquid was forced out between the crucible and the die, underneath the tight

fitting stainless steel sleeve, and deposited itself on the lower portion of the furnace windings.

3. Un-cooled Die; Pressure Forced.

A graphite crucible with a .050" vertical slot in the bottom was used in this procedure. The crucible was suspended from the top of the furnace. The same piston assembly described in procedure (2) was set in place above the crucible. A silica tube of 2 1/2" outside diameter and 36" long was sealed at its lower end and filled to within 3" of the top with water, and then placed below the furnace. The rollers were removed from below the furnace to permit placing of the tube. A stainless steel spacer and graphite supporting piece were installed below the crucible to the bottom of the furnace to protect the furnace windings from any splashing of molten aluminum. The furnace temperature was brought up to 740°C and stabilized. Before lowering the piston onto the top of the melt, the silica tube was raised into the furnace to the bottom of the crucible. The piston was then lowered to bear on the top of the melt, which was forced through the slot in the bottom of the crucible directly into the water.

The intent of this procedure was to force the molten alloy through the slot, to be quenched in the water in a continuous, thin sheet form.

This procedure also did not produce a thin strip of alloy. The melt was forced through the die slot in the base of the crucible, but upon striking the water surface it formed into irregular nodules or circular, concave, dish shaped units rather than the strip form. The nodules were generally found to be at least partially hollow. Because of the position of the crucible base and water surface well up within the furnace, the form of the molten alloy after leaving the die and before striking the water could not be observed.

4. Un-cooled Die; Strip Initiated.

The same, top supported, crucible used in procedure (3), as well as several subsequently fabricated ones of similar construction, was used in this procedure. The motor driven rollers were replaced below the furnace. A strip of 0.010" carbon steel shim stock was threaded through the slot at the bottom of the crucible and between the rollers. About 18" of strip extended above the crucible slot. Water tubing, was run to play a stream of water on the rollers, the water being collected in a basin below.

The intent of this procedure was to have the molten alloy wet the steel strip and form a more or less uniform layer on the surfaces of the strip as it was pulled down through the slot by the rollers below. The strip would then be cooled by playing water upon it as it emerged from the furnace, thus cooling and solidifying the molten

alloy uniformly as it passed from the furnace.

The furnace was energized and temperature stabilized at 740°C. The water and rollers were then started and the strip pulled down at speeds varying between 10 and 50 cm./hr.

In a subsequent employment of this procedure, a flux ("METAL FLUX", formula 162, manufactured by AIR REDUCTION CO.) was sprinkled on the steel strip and fused by heating before insertion into the crucible and furnace in an attempt to achieve better wetting of the steel strip. Stainless steel shim stock was also used for the strip subsequently.

This procedure also failed to produce a coherent strip of alloy which could be cooled directionally. Very poor wetting of the steel strip by the molten alloy was experienced in all cases. With the carbon steel strip there was some adherence by the melt to the flaky oxide film which covered the strip as it passed through the crucible in the furnace above the melt. When the steel strip was fluxed, no adherence was observed although the flux did prevent the oxide layer from forming. Slightly better wetting was experienced with the stainless steel strip but yet no coherent alloy layer was formed on the strip. Metallographic specimens taken from the aluminum-nickel alloy deposited on the oxide covering of the carbon steel strip and from the stainless steel

strip show a generally dendritic form of the Al_3Ni compound with axes in various orientations. A major portion, however, was aligned at an angle toward the strip face. (See Figure I)

5. Directional Solidification Within Mold.

In an effort to verify that the desired fibrous structure could be formed at higher growth rates, an appratus similar to that used by Mallard and Flemings[1] was constructed. The alloy source for this procedure was 0.25 in. diameter rods of 6.13 wt. % Ni which were swaged to a diameter of 1/8 in. A chromel-alumel thermocouple in a protective tube was then laced alongside and near one of the ends of one of the Al-Ni rods with wire. This assembly was then placed inside a silica tube, about 18 in. long and .425 in. O.D The remainder of the silica tube was then filled with powdered graphite and tamped down tightly. A chromel wound resistance furnace was fabricated around a piece of silica tube of the same diameter, using asbestos sheet and fiber as insulation. A cylindrical, copper water-cooling chamber was also constructed to fit closely below the furnace. The same DC motor and gearbox that was used to drive the rollers previously was re-rigged to be capable of pushing the silica tube downward through the furnace and cooling chamber.

The procedure was started with the silica tube extending through the furnace and cooling unit, and extending slightly below the

LONGITUDINAL SECTION OF Al-6.3 Wt. % Ni ALLOY DEPOSITED ON STAINLESS STEEL STRIP. FACE OF STRIP IS PERPENDICULAR TO RIGHT SIDE OF PHOTOGRAPH. (435X)

FIGURE I.

cooling unit. The thermocouple leads extend from the bottom of the silica tube to a potentiometer. In this position the thermocouple within the tube should be well up within the furnace. When the furnace temperature was stabilized, the motor drive was started at a predetermined speed. The thermocouple would then be driven down into the cooling chamber and the temperature gradient recorded. This would be repeated until the desired temperature gradient was achieved by altering the furnace temperature.

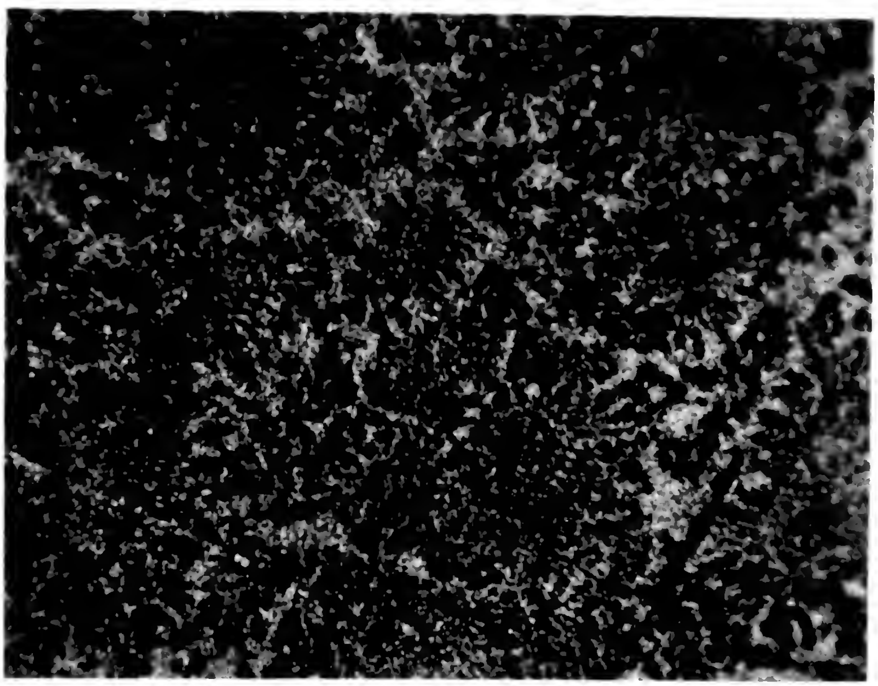
This procedure yielded a metallographic specimen of good fiber alignment. This sample was grown at a rate of 95 cm./hr. Low temperature readings from the thermocouple prevented ascertaining the gradient which was achieved. The low readings resulted from placing the thermocouple too low in the silica tube when it was prepared. When the tube was inserted in the furnace and cooling chamber, the area in the vicinity of the thermocouple was either too close to, or within the cooling chamber. Tests of the furnace alone after its fabrication demonstrated its ability to attain a temperature of 1000°C at 1.75 amperes which was the current held during this run. The above mentioned growth rate proved to be the slowest which could be attained with this motor-gearbox combination without stalling the motor.

Metallographic study of this sample showed a cellular structure

in cross-section, the cells being composed of a well aligned and very fine fiber structure. The cell boundaries were characterized by a coarsening of the fibers. Fiber spacing within the cells was 0.9 microns as measured from a longitudinal section. A tensile specimen was made of the portion of rod remaining after metallographic specimens were taken. The specimen fractured at the cite of a gas hole extending in excess of one-half of the cross-sectional area. The load at failure based on the diameter of the rod alone was 10,000 PSI, however.

Further use of this apparatus was prevented by burning out of the furnace windings on the second run.

LONGITUDINAL SECTION OF COMPOSITE GROWN BY PROCEDURE 5.
GROWTH RATE 95 CM./HR. (1100X)



CROSS SECTION OF ABOVE SHOWING CELLULAR STRUCTURE (700X)

FIGURE IV.

III. DISCUSSION OF RESULTS

Although the procedure of drawing a thin strip of alloy from a cooled die while directionally solidifying it did not prove successful in this work, the striking success at achieving a composite structure at the high growth rate of procedure (5) indicates that the continuous die casting process shows great promise. The problems encountered with this procedure and that employing the piston with the water cooled die are believed to be due to the geometry of the elements and their position within the furnace. The water cooled die represents an appreciable mass of which only about 1/2 inch extended far enough into the furnace to be abreast of the lower extremeties of the heating coils. The problem then was the freezing of the melt at the entrance of the die. It would be possible to extend the die to further up into the furnace, but then the attainment of the desired gradient may prove much more difficult. A possible solution would be to construct a die of two elements; the upper being uncooled and higher up in the furnace than previously. The lower, cooled portion would be thermally insulated from the upper and possibly extend slightly into the furnace. This arrangement should provide a sharp thermal gradient and also allow the melt to assume a thin strip form in the die before solidification. Sufficient heating capacity would have to be provided however to maintain the temperature

of the molten alloy in the upper portion of the die despite the high conductivity of the melt. Paralleling this, the furnace should also be capable of attaining a higher maximum temperature.

The metallographic specimens studied of that alloy which was deposited on the steel strips indicate that the direction of heat flow was generally into the steel from the molten alloy. This was most likely a result of failure to supply a uniform conduction path through the alloy. If this were provided, the higher conductivity of the alloy should cause directional solidification along the strip. The stainless steel strip offered the most promise of attaining uniform wetting. To accomplish this, a more accurately fitted strip and die slot combination would probably be required as well as higher melt temperature. Either drawing the strips up through the melt rather than down, or drawing them horizontally through the melt would probably eliminate the globular formation which much of the alloy assumed on the strip after passing through the die. The direct use of water as a coolant would be inappropriate if the strip were drawn vertically upward through the melt and more difficult if done horizontally however.

The formation of the concave, dish-shaped units when the melt was forced through the die directly into water was probably caused by the force of steam generated beneath the drop of molten alloy when it struck the water. The drop would flatten upon striking the water and the steam pressure would force the center upward. The

hollow globular forms most likely resulted from larger drops which did not flatten out sufficiently to contain the steam pressure beneath but did dissociate hydrogen from the water and build up hydrogen pressure within. Shrinkage upon freezing would also contribute to the hollowing effect. These results indicate that generally a steady stream of molten alloy did not leave the die. On two occasions however a much larger, very irregularly shaped, globular mass resulted indicating that probably a more or less steady stream was forced through the die. This effect of the water on the molten metal causes this method of production to appear to be the least promising of those attempted.

The achievement of a composite structure by Procedure (5) at a growth rate of 95 cm./hr. is extremely encouraging for prospects of efficient production of eutectic composites. The temperature gradient achieved in this case may be estimated. During tests of the furnace after its fabrication, it attained a temperature of 1000°C to within about 3 cm of each end at the current used during production of the sample. Assuming that the sample was cooled to 50°C at the upper seal of the cooling chamber would indicate a gradient of about 300°C/cm. and the G/R ratio would then be about 3.16 (°C-hr./cm.^{2}). Hertzberg, Lemkey, and Ford[5] used a constant average gradient of about 31°C/cm. to form Al-Al_3Ni composites at varying growth rates up to 28.7 cm./hr. indicating that a G/R ratio

of only about 1.1 $^{o}C-hr./cm.^{2}$ would be required to form this composite.

The cellular structure, Chilton and Winegard[7] have shown, is caused by impurities in eutectics by producing a curved, cellular solid-liquid interface. This type of cellular structure was also experienced by Hertzberg, Lemkey, and Ford[5] however in most of the specimens which they grew at the higher rates (11.2 to 28.7 cm./hr.).

Lemkey, Hertzberg, and Ford[2] compared the fiber spacing of $Al-Al_3Ni$ composites which were grown at varying rates and confirmed that the spacing varies with the inverse square root of the growth rate. Extrapolation of their data (maximum rate was 19 cm./hr.) predicts a fiber spacing of about 0.65 microns for a growth rate of 95 cm./hr. The spacing of 0.9 microns measured in this sample then is in fairly good agreement.

This type of apparatus would be easily adaptable to a continuous casting process by providing a reservoir of molten alloy above the mold and drawing the solidified composite out of the bottom of the mold at the proper rate. A more durable mold material than the packed graphite would be required. Consideration of the lower G/R ratio apparently required to form this composite indicates that considerably higher growth rates may be employed with this apparatus. A similar type of apparatus is easily envisioned for producing the composite in sheet or strip form.

IV. CONCLUSIONS

A study was made of methods for producing a fiber eutectic Al-Al_3Ni composite at high rates of growth.

Continuous casting of fiber eutectic structures as thin strip or small diameter rods at high rates of growth has been demonstrated to be feasible. Growth of fiber eutectic at 95 cm./hr. with a liquid temperature gradient of about $300^{\circ}C/cm.$ produced a fine fiber structure with a fiber spacing of 0.9 microns. Cellular growth which is observed is probably due to impurity segregation during freezing.

Attempts at casting a thin eutectic fiber strip from a large reservoir were not successful. The large temperature gradient required caused the metal to freeze at or near the bottom of the liquid metal reservoir. Continuous drawing of the strip was not possible.

V. RECOMMENDATIONS

1. That further experimental work be carried out at higher growth rates with the apparatus of procedure (5) under a range of controlled temperature gradients.

2. That the mechanical properties of the specimens produced at these higher growth rates be determined.

3. That a die casting apparatus similar to that used in procedure (1) be designed and built to provide the required temperature and temperature gradient for further investigation of the feasibility of this form of production.

APPENDIX

DESCRIPTION OF APPARATUS

Furnace Utilized in Procedures 1 through 4.

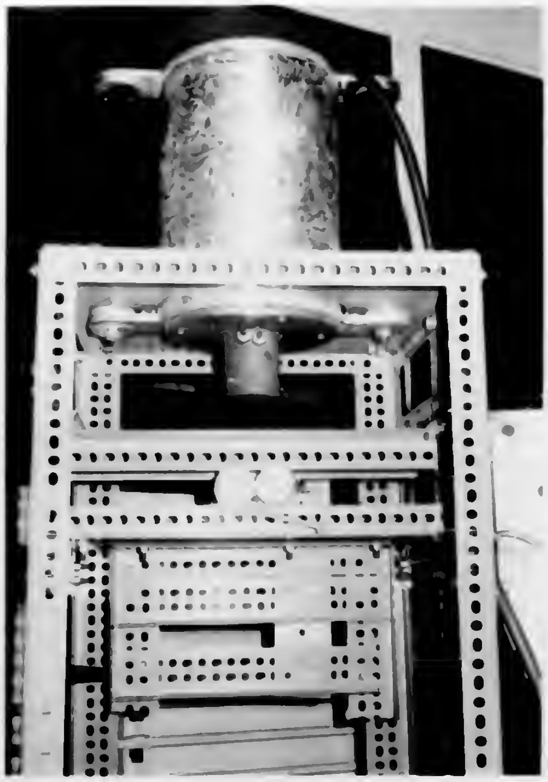
Heating Element: 2 sets of vertical coils mounted one atop the other. Rated capacity 9 amps @ 115 volts for each coil (1000°C).

Furnace Box : Vermiculite between stainless steel cylinder and heating element. Insulation jacket of two layers of aluminum foil, 2 layers of asbestos cloth and one layer of spun glass around cylinder.

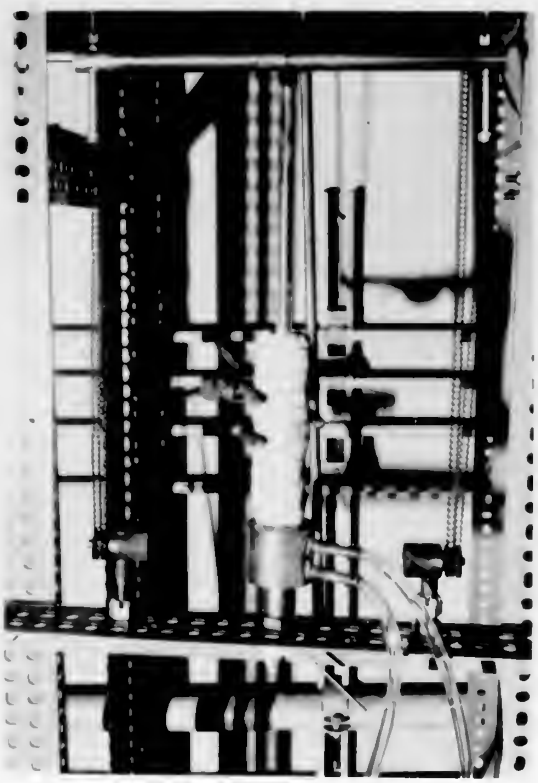
Temperature Controls: Variac to control furnace current. Thermocouple inserted into furnace wall (range 0 to 1000°C).

Cooling Chamber for Procedure 5.

Fabricated from 2" diameter copper bar. A cooling water cavity was machined into the interior and O-ring grooves at each end. A flat washer-shaped O-ring compressor was used to seal the upper end and allow close mating with the furnace. A bored, plug-type threaded compressor was used for the lower O-ring seal. (See Figure V.)

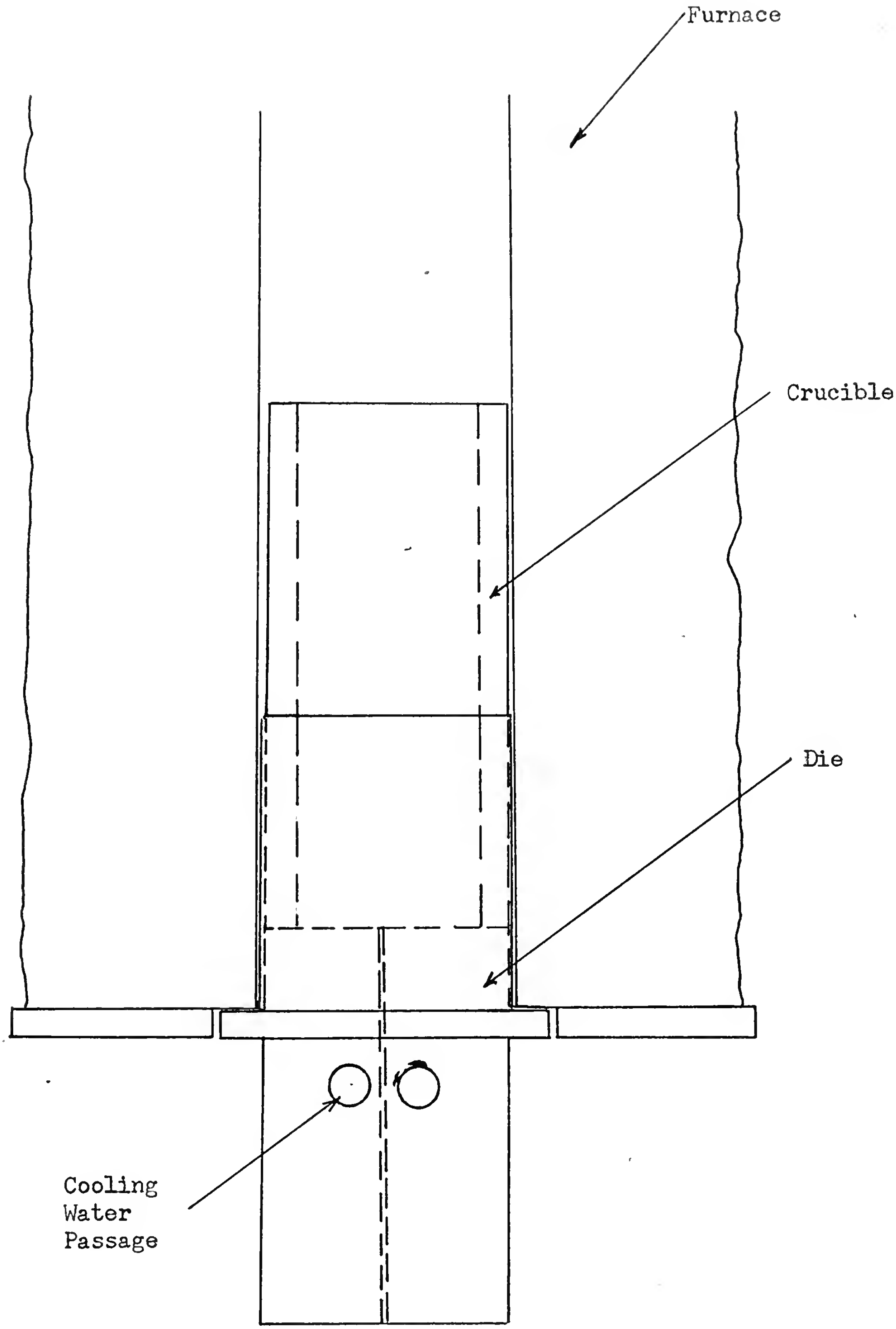


Apparatus For Procedures 1 and 2. (Furnace Used For Procedures 1-4)



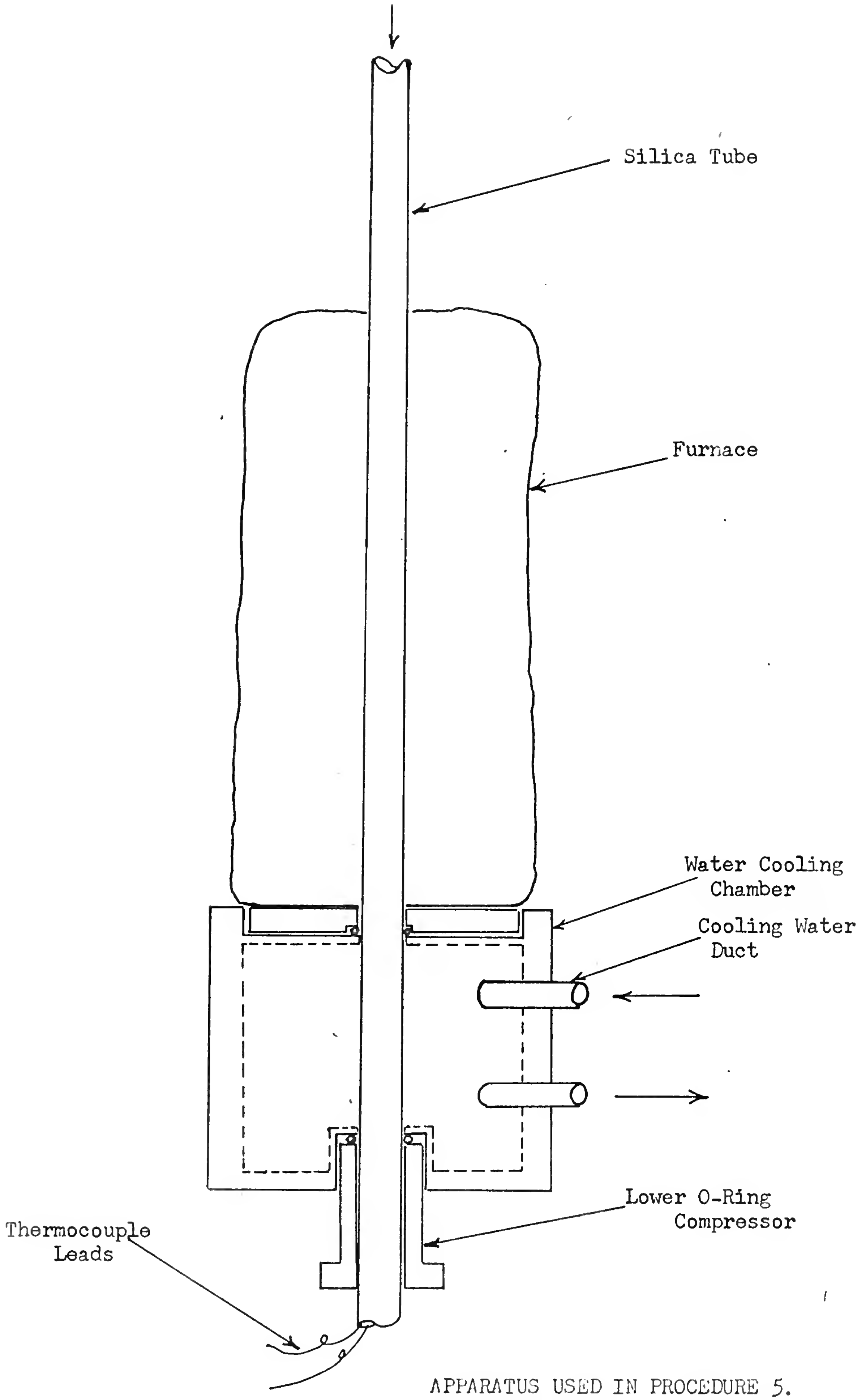
Apparatus Used in Procedure 5

FIGURE III.



APPARATUS USED IN PROCEDURES 1 & 2

FIGURE IV.



APPARATUS USED IN PROCEDURE 5.

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